MAX-PLANCK-INSTITUT
FÜR KOLLOID- UND
GRENZFLÄCHENFORSCHUNG

12. PHOTOCHEMISTRY OF TM COMPLEXES

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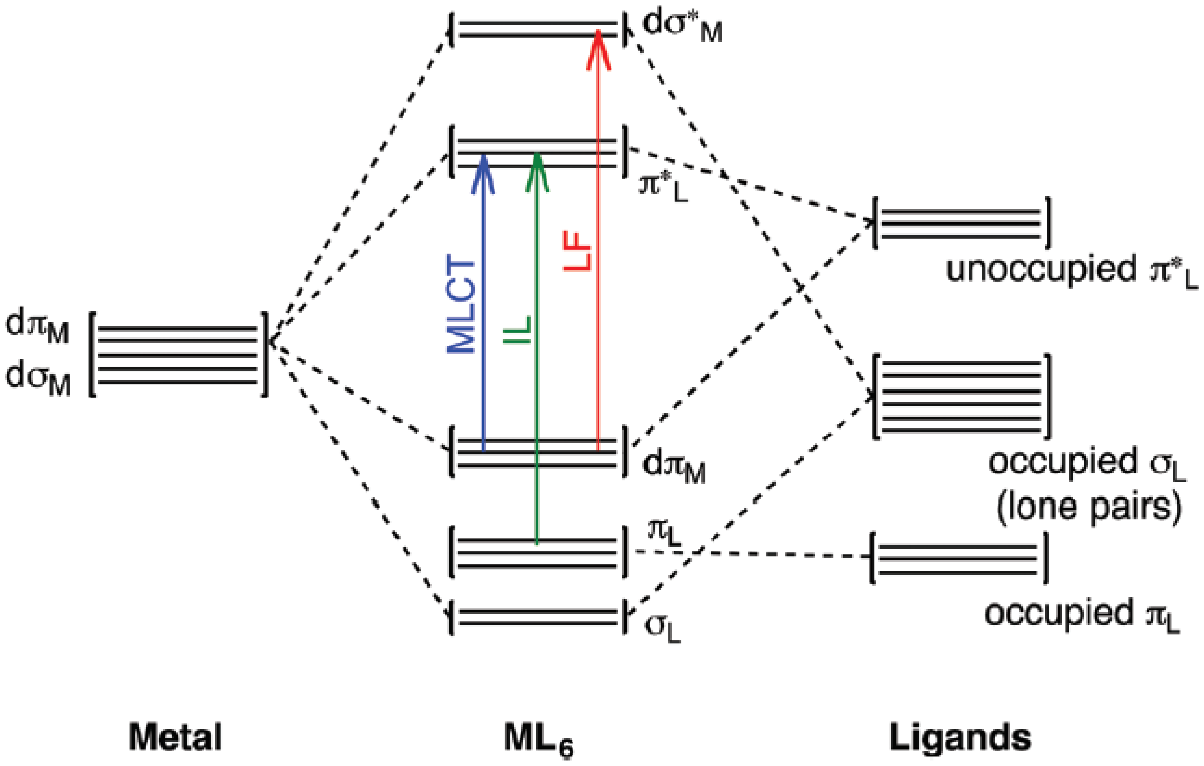
12.1.1 GENERAL OVERVIEW

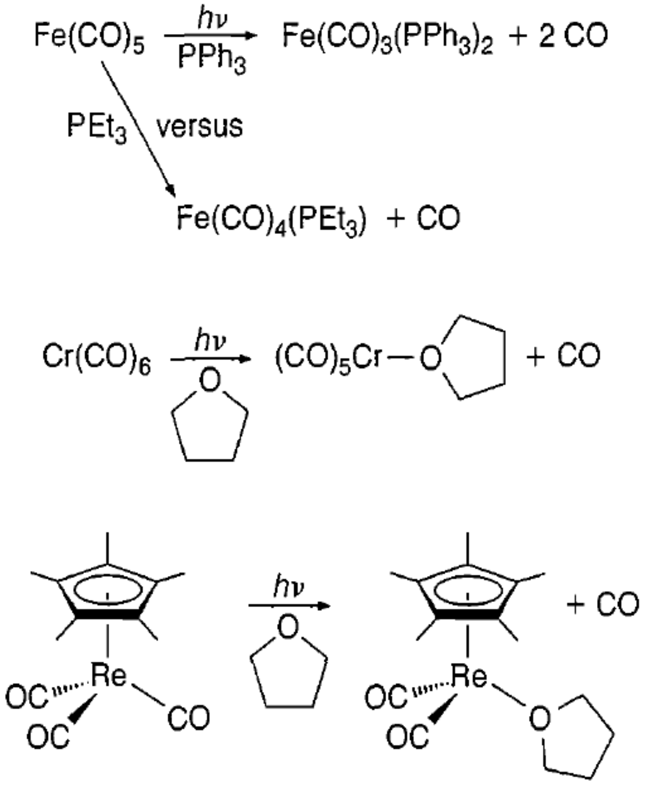


octahedral complex w/ π-accepting ligands (like fac-Ir(ppy)$_3$, Ru(bpy)$_3$…)

Arias-Rotondo *Chem Soc Rev* **2016** 45, 5803. DOI: 10.1039/C6CS00526H
MacMillan *Chem* Rev **2013** 113, 5322. DOI: 10.1021/cr300503r

12.2.1 LIGAND PHOTODISSOCIATION

- For better control of stoichiometry in ligand substitution (i.e. further substitution of THF after photolysis)
- Most common CO dissociation (usually w/ UV)
- Used to be considered a ligand-field d-d transition (unoccupied d to σ*) -> weakening M-L bond…



12.2.2 LIGAND PHOTODISSOCIATION MECHANISM

Actual mechanism is more complex

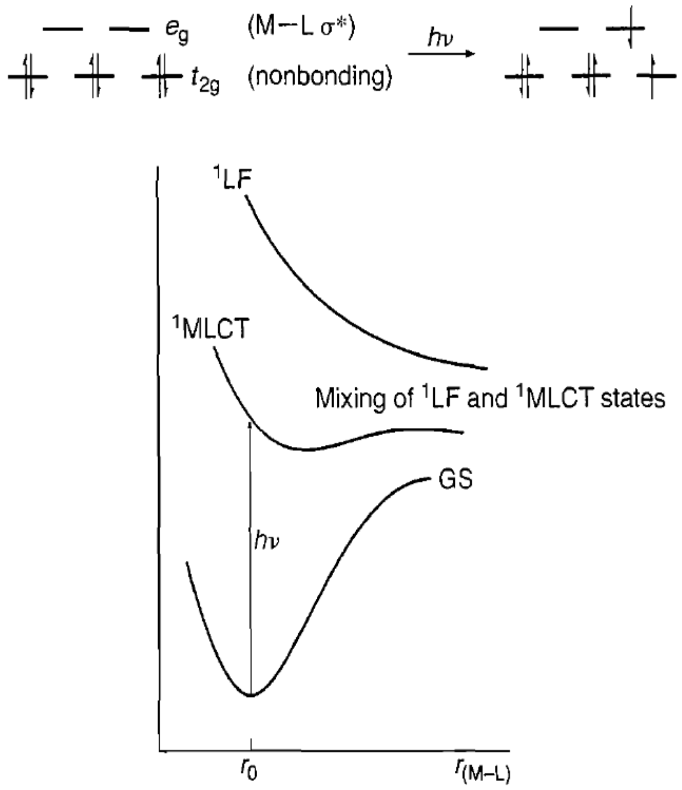


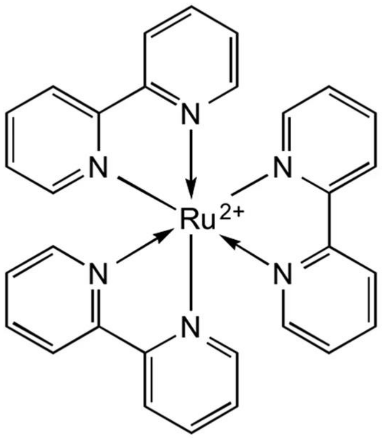
Figure 5.6.
Top: Electron promotion initially thought to occur upon photolysis of an octahedral d^6 complex. Bottom: Mixing of excited states that are now thought to more accurately reflect the events that occur after photolysis of metal–carbonyl compounds, such as $M(CO)_6$ (M = Cr, Mo, and W).

12.3.1 POD1

$Ru(bpy)_3(PF_6)_2$ is one of the most common photoredox catalyst.

a) Provide the oxidation state, d-electron count, and overall electron count for this complex.

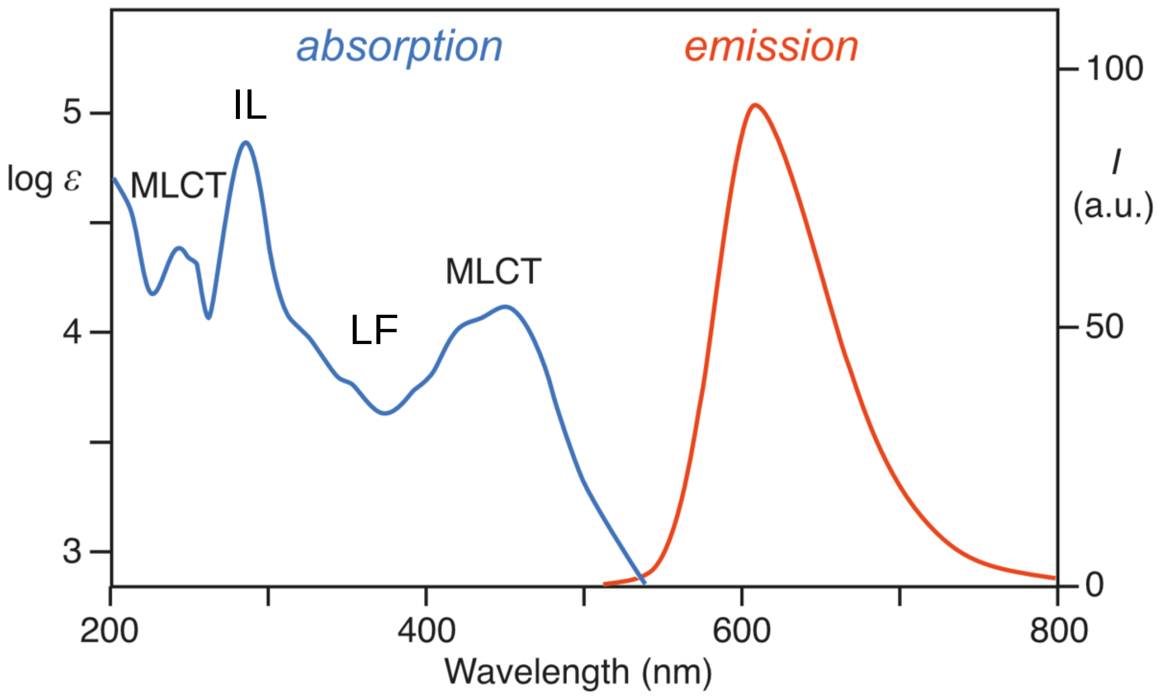
b) Propose a synthesis of this complex from inexpensive commercially available starting materials.



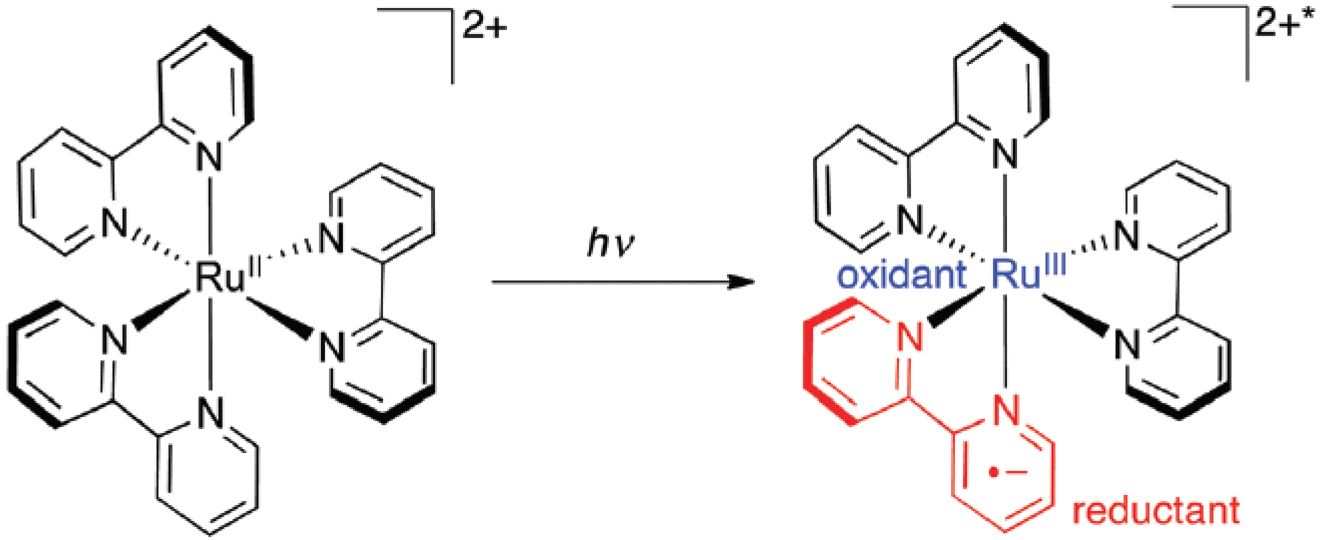
Photochemical Properties
Absorption λ_{max}: 454 nm
ε = 14,600 M^{-1} cm^{-1}
Excited State: ^{3}MLCT
Triplet Energy: 2.12 eV
τ_0 (MeCN): 1100 ns
Emission λ_{max}: 605 nm

Redox Properties
$E_{1/2}$ (Ru^{2+}/Ru^{3+}) = +1.29 V vs. SCE
$E_{1/2}$ (Ru^{2+}/Ru^{+}) = -1.33 V vs. SCE
$E_{1/2}$ ($Ru^{3+}/{}^*Ru^{2+}$) = -0.81 V vs. SCE
$E_{1/2}$ ($^*Ru^{2+}/Ru^{+}$) = +0.77 V vs. SCE

12.3.2 $Ru(bpy)_3$ ABSORPTION BANDS



12.3.3 Ru(bpy)$_3$ – EXCITED STATE



Arias-Rotondo *Chem Soc Rev* **2016** 45, 5803. DOI: [10.1039/C6CS00526H](10.1039/C6CS00526H)
MacMillan *Chem* Rev **2013** 113, 5322. DOI: [10.1021/cr300503r](10.1021/cr300503r)

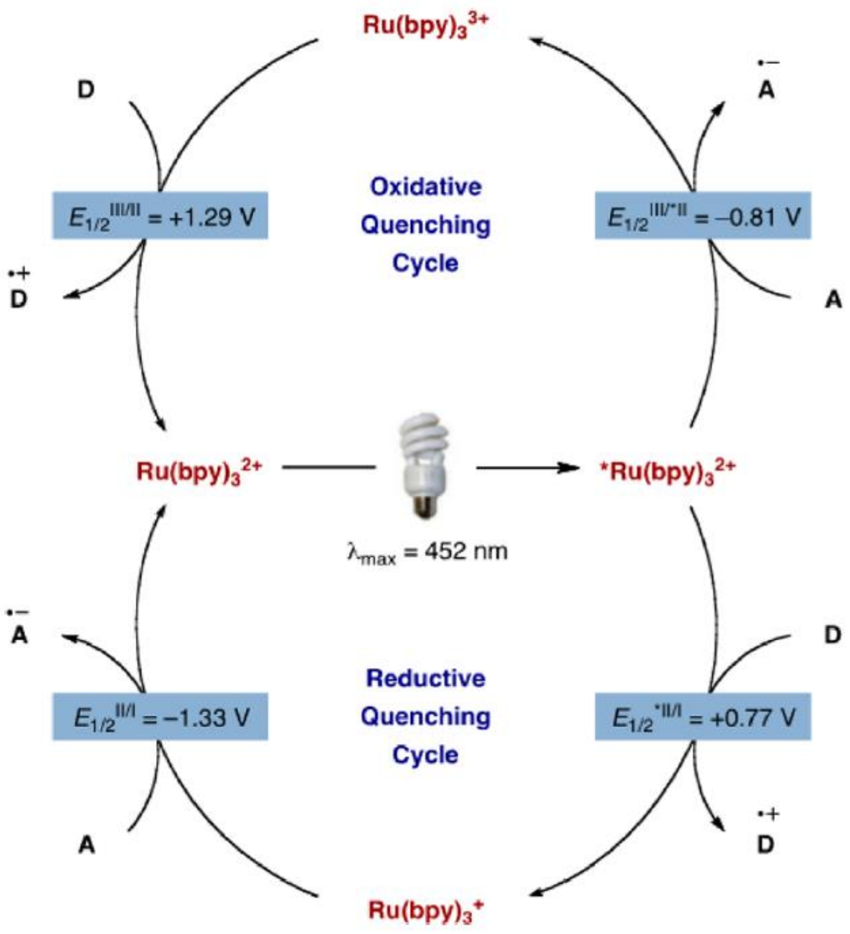
12.3.4 $Ru(bpy)_3$ – PHOTOCHEMISTRY

Oxidative quenchers:

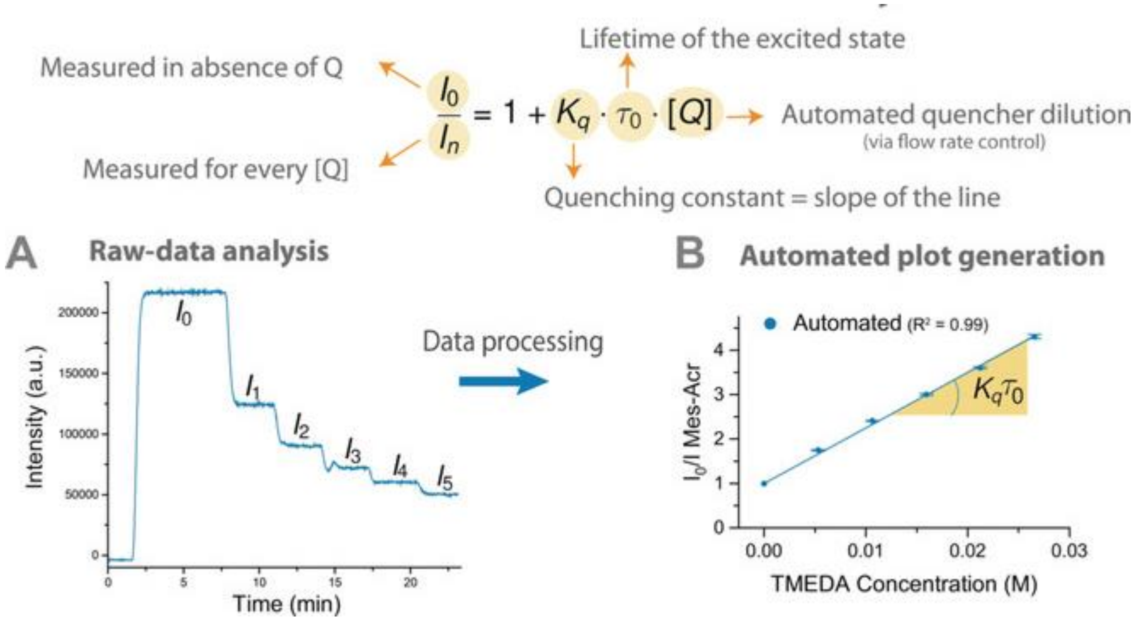
viologens, polyhalomethanes, dinitro- and dicyanobenzenes, and persulfate

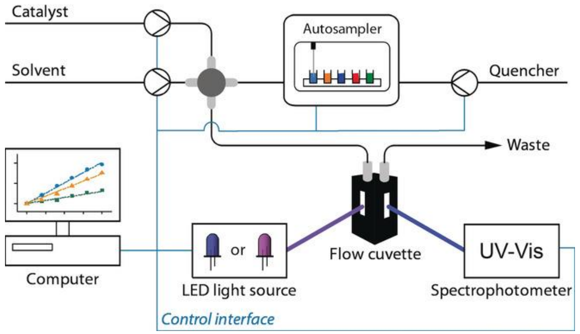
Reductive quenchers:

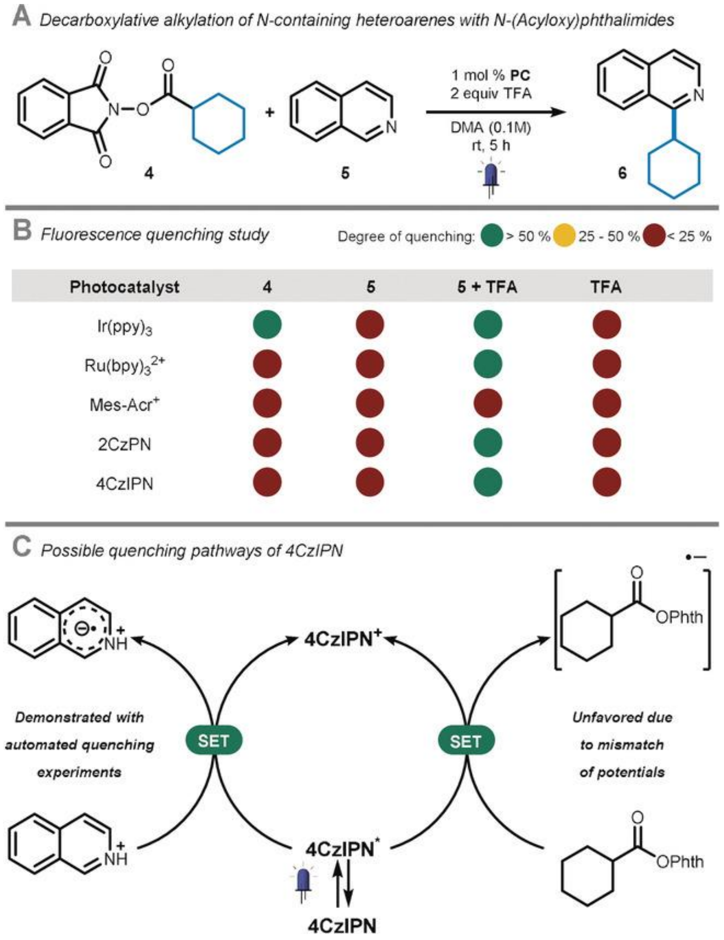
tertiary amines



12.3.5 EXCITED STATE QUENCHING – STERN-VOLMER ANALYSIS



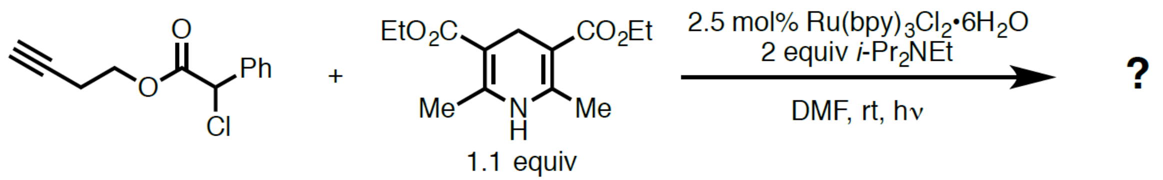


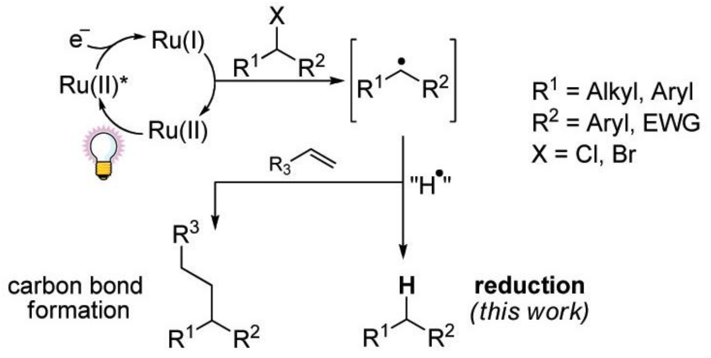


Noel *ACIE* **2018** 57 11278. DOI: 10.1002/anie.201805632

POD #2

For the reaction below, **predict the product(s) and propose a plausible mechanism.**

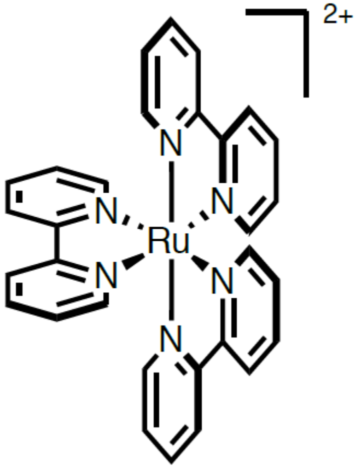




Stephenson *JACS* **2009**, *131*, 8756. DOI: 10.1021/ja9033582

POD #3

Consider the following three octahedral ruthenium(II) complexes. **Order them in terms of excited state reduction potential.**



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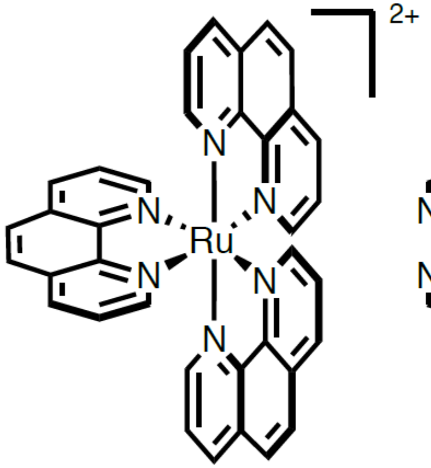

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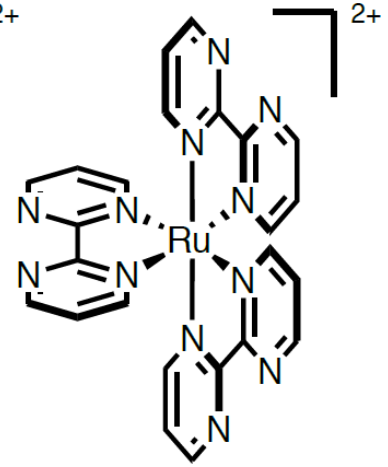
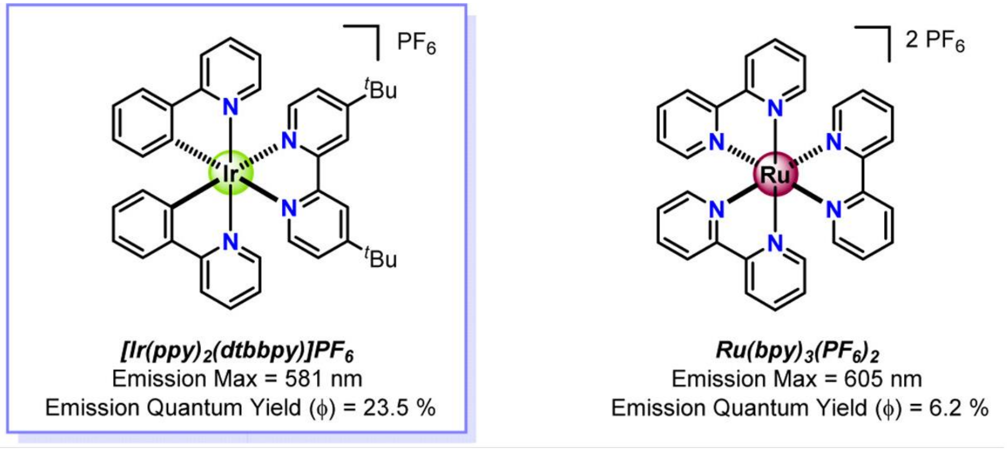
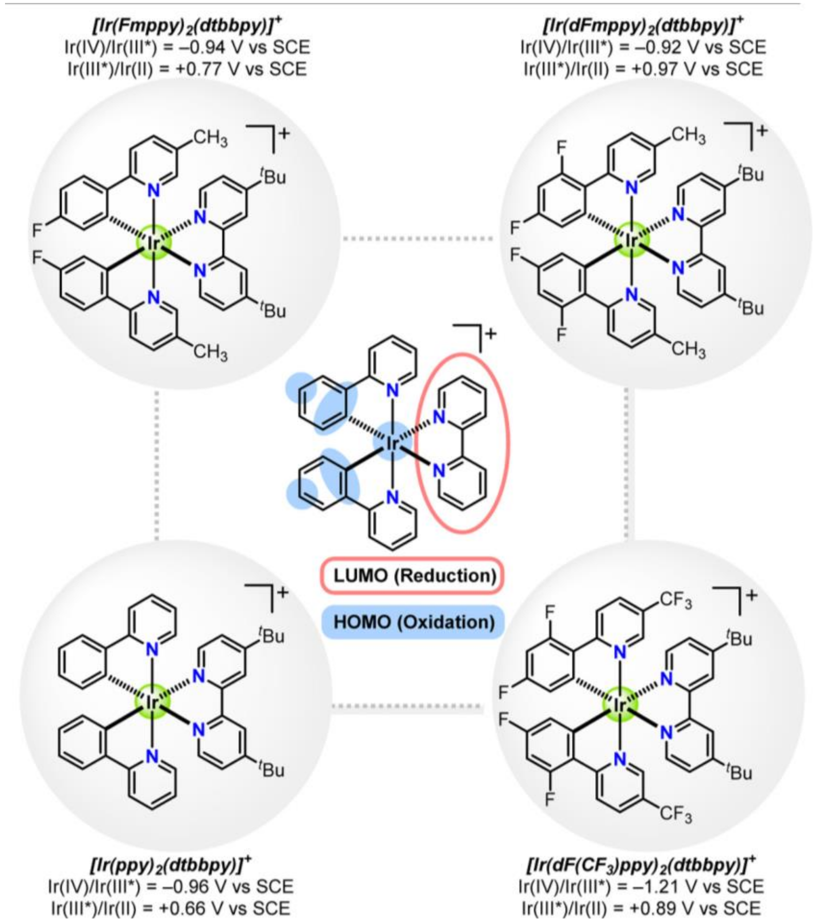


1

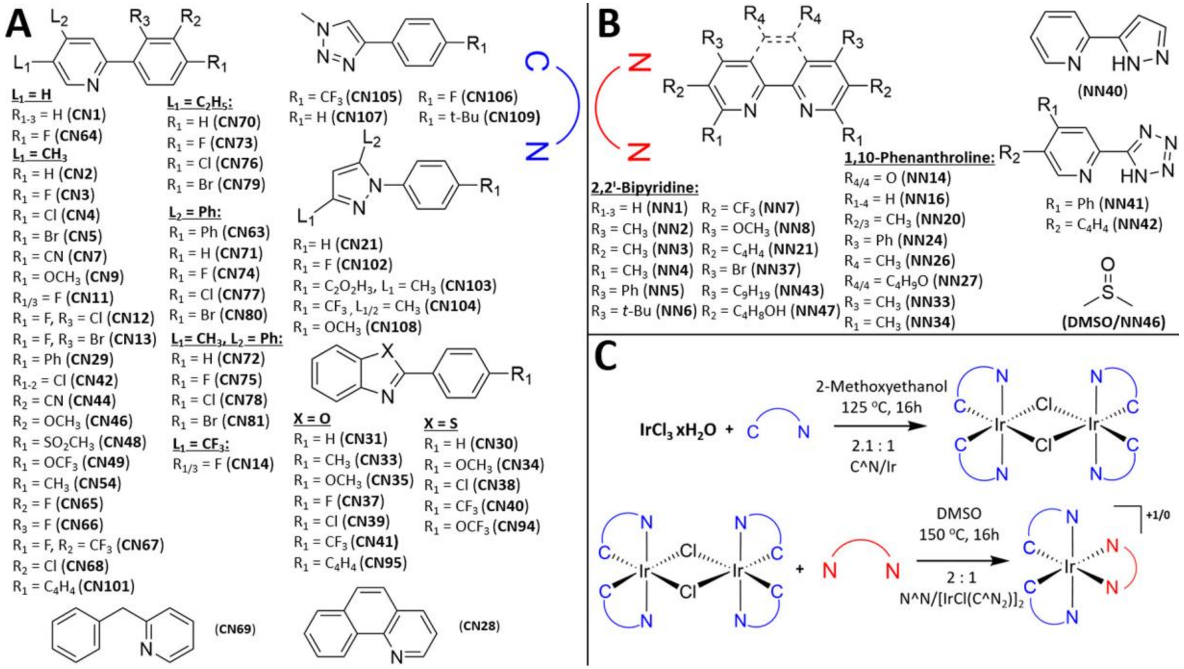
- EWG -> more oxidizing
- EDG -> more reducing

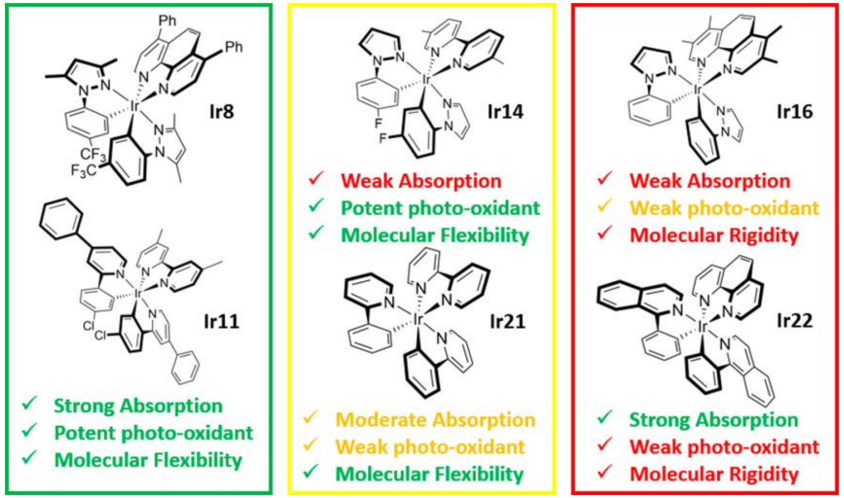
12.3.5 HETEROLEPTIC Ir PHOTOCATALYSTS





12.3.5 HETEROLEPTIC Ir PHOTOCATALYSTS

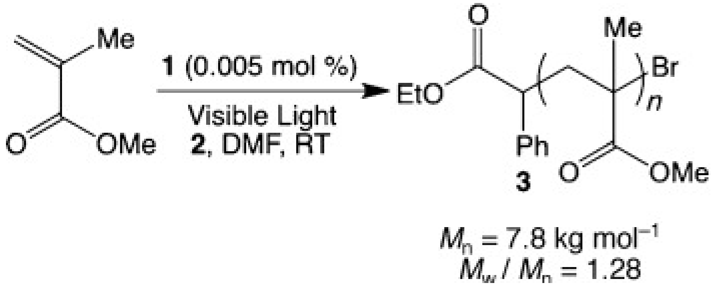


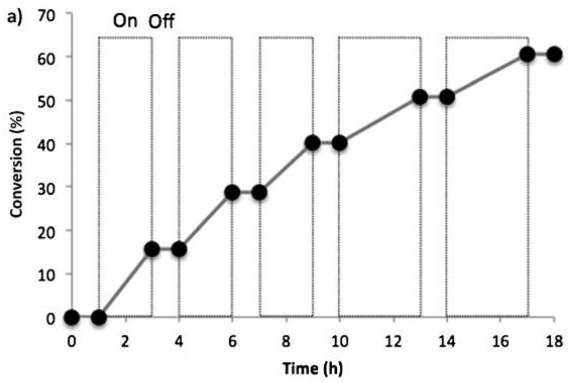


Bernhard, *JACS* **2022** 144, 1431. DOI: 10.1021/jacs.1c12059

12.3.5 PHOTOPOLYMERIZATION

Photochemistry for spatio-temporal control of reaction -> polymerization

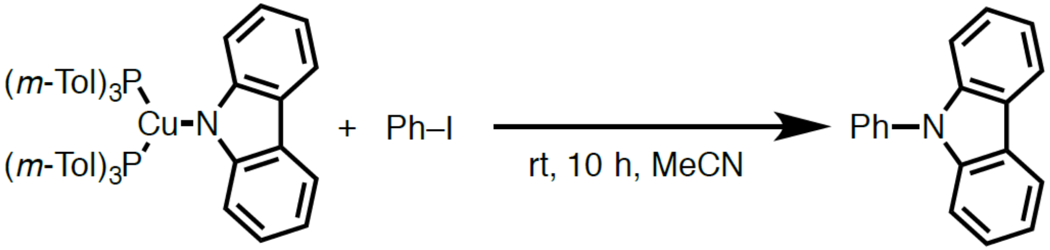




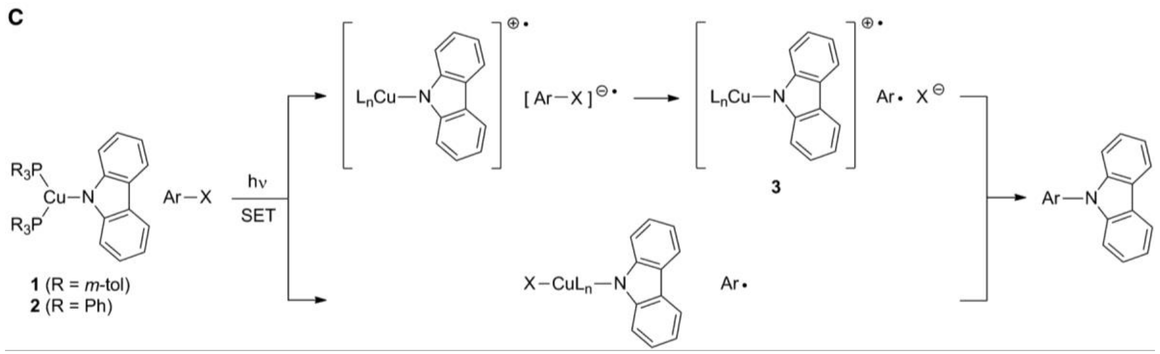
Hawker *ACIE* **2013** 51, 8850. DOI: 10.1002/anie.201203639

POD 4

For the transformation below, **propose a role of light in the reaction.**

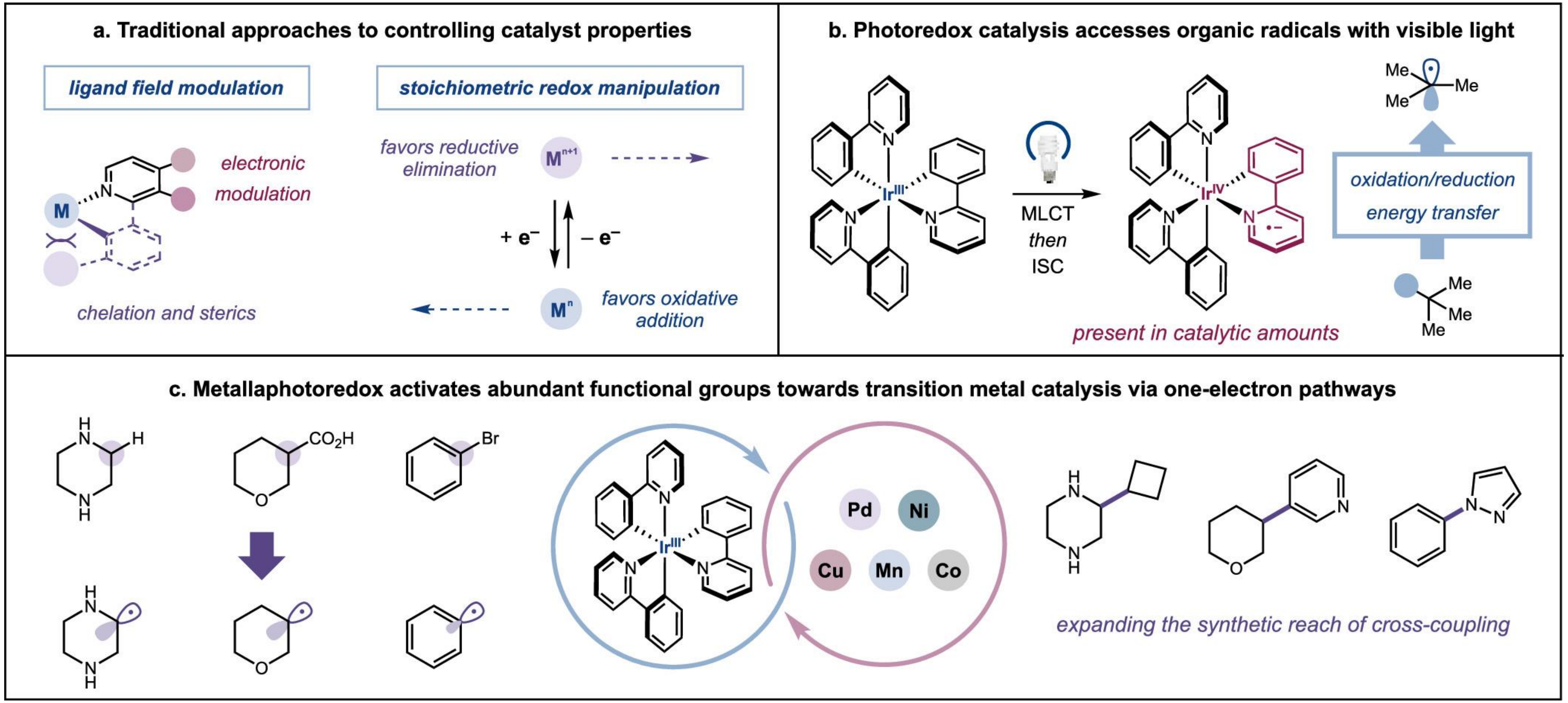


hν (13-watt CFL): 74% yield
dark: <1 % yield



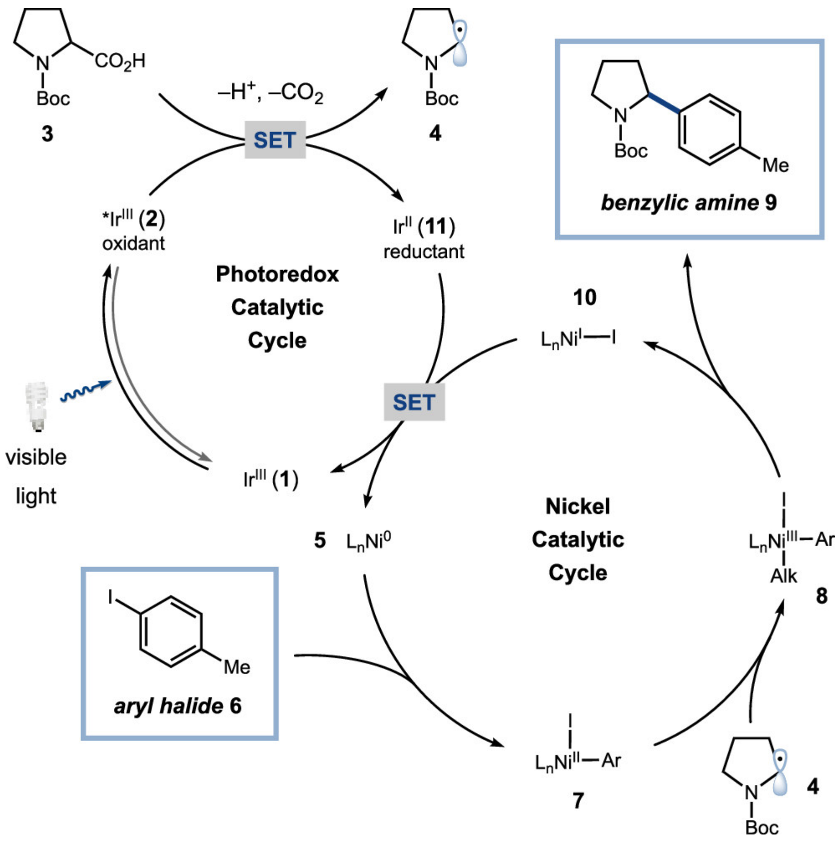
Fu *Science* **2012**, *338*, 647. DOI: 10.1126/science.122645

12.4.1 METALLAPHOTOREDOX



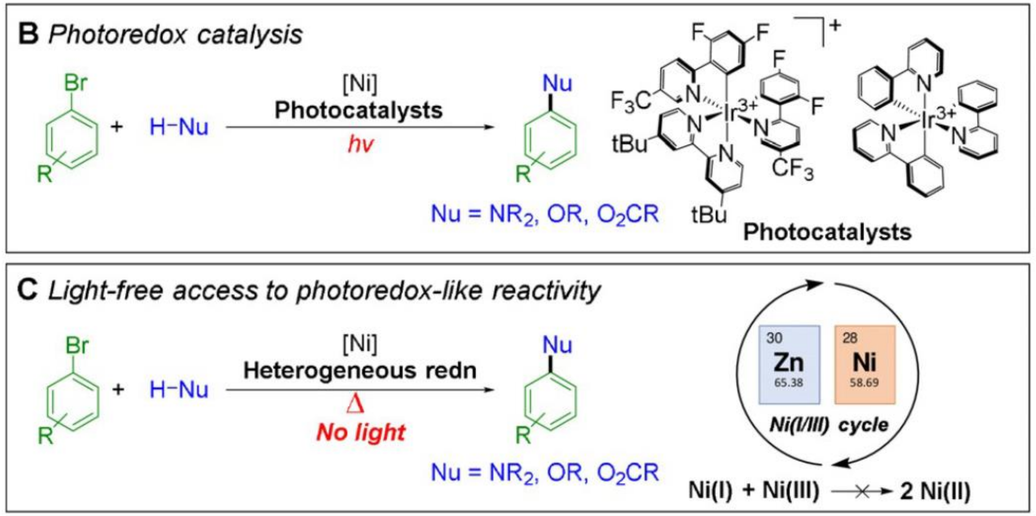
MacMillan *Chem Rev* **2022**, 122, 1485. DOI: 10.1021/acs.chemrev.1c00383

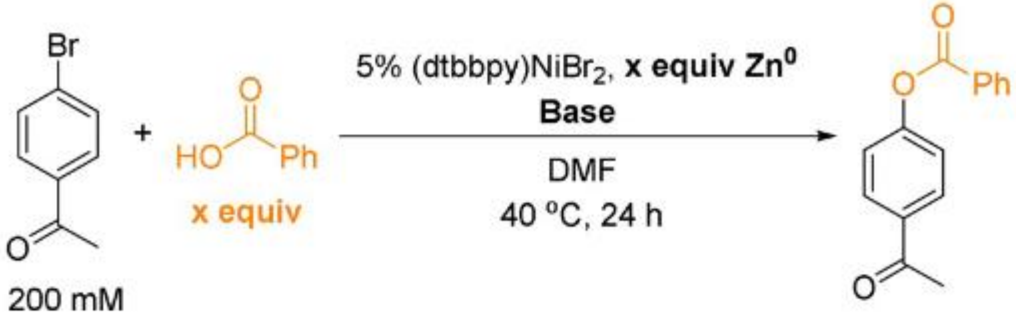
12.4.1 METALLAPHOTOREDOX

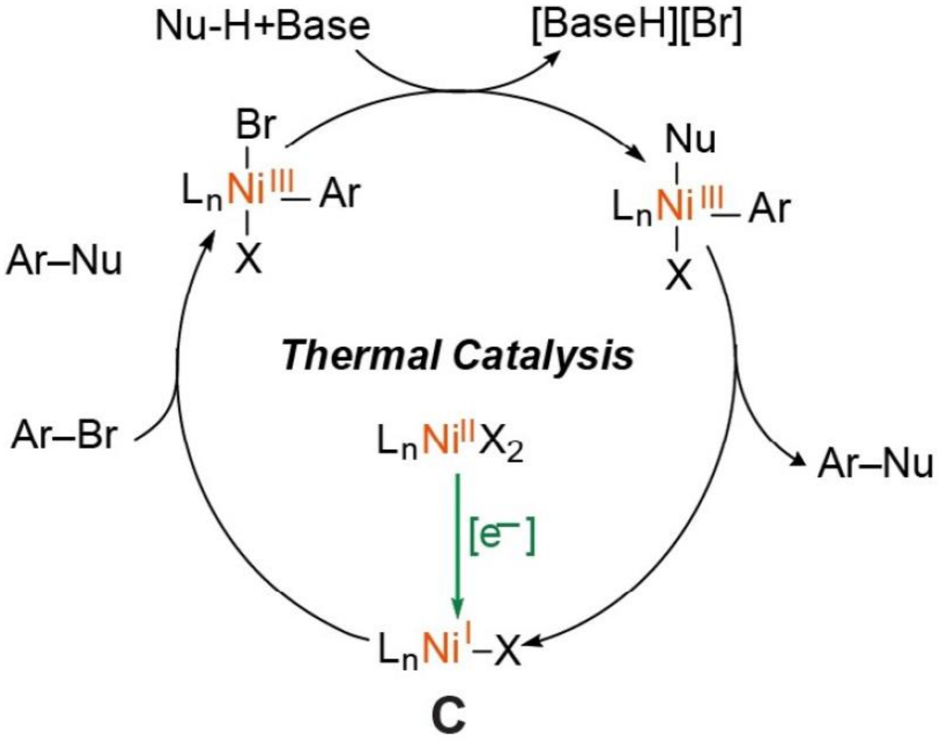


MacMillan *Chem Rev* **2022**, 122, 1485. DOI: 10.1021/acs.chemrev.1c00383

12.4.2 NICKEL: FROM PHOTO- TO THERMAL CATALYSIS

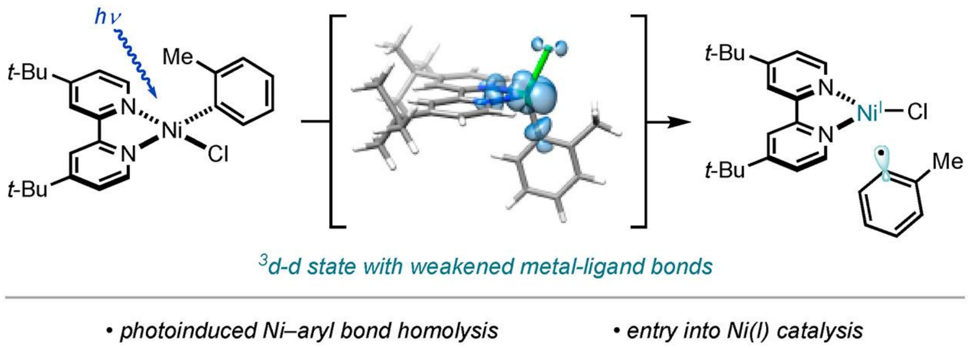


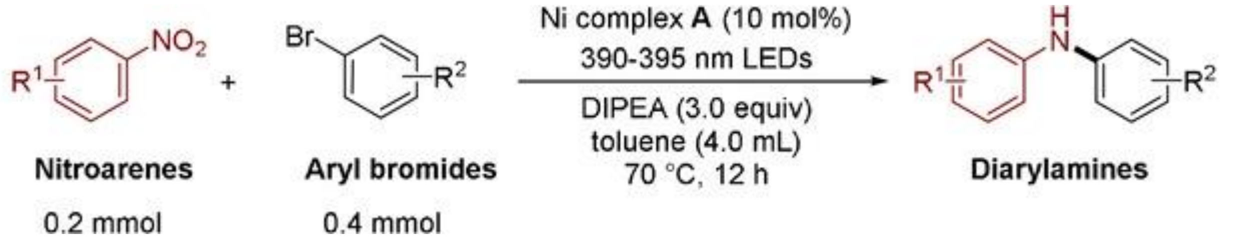


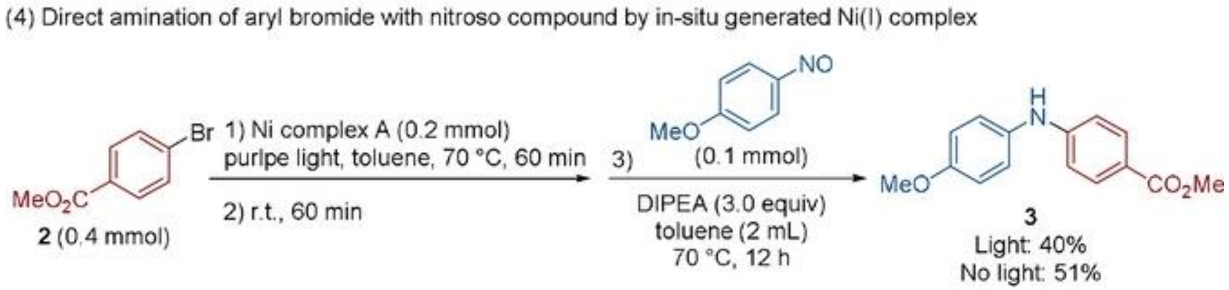


Nocera *ACIE* **2020** 59, 9527. DOI: 10.1002/anie.201916398

12.4.2 NICKEL: FROM PHOTO- TO THERMAL CATALYSIS

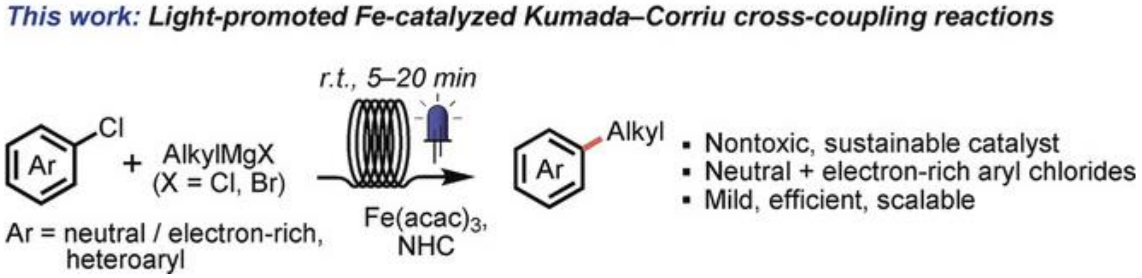


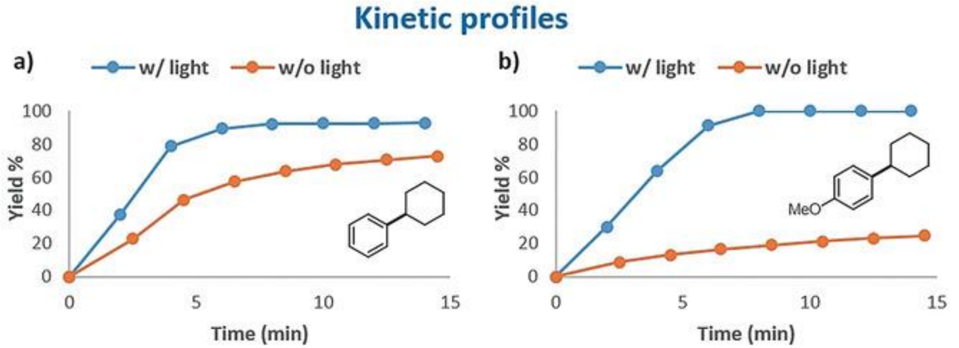


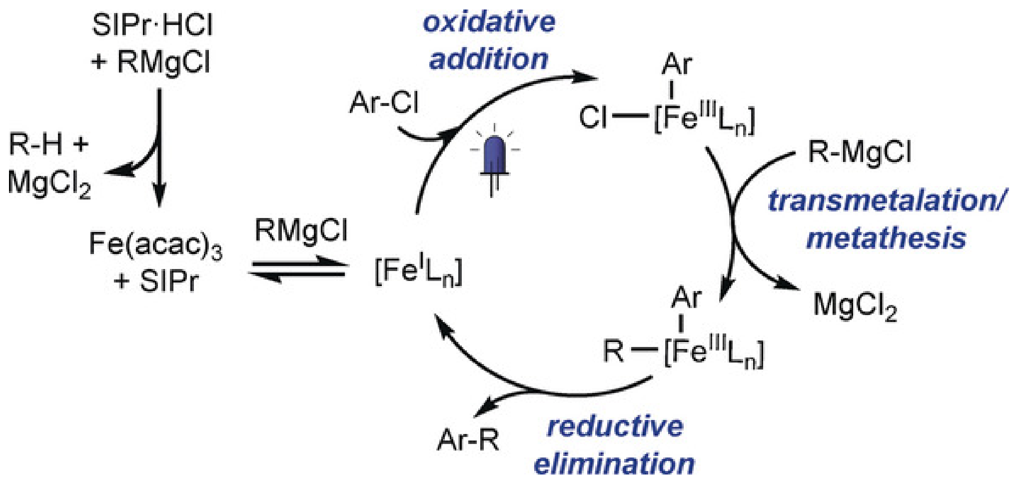


Doyle *JACS* **2020** 142, 12, 5800. DOI: 10.1021/jacs.0c00781
DOI: 10.1002/anie.202012877

12.4.3 PHOTO-PROMOTED KUMADA







Noel ACIE **2019** 58 13030. DOI: 10.1002/anie.201906462